Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Light-enhanced Oxygen Degradation of $MAPbBr_3$ Single Crystal

Ke Wang[1], Benjamin Ecker[1], Maitrayee Ghosh[2], Mingze Li[3], Valentin V. Karasiev[2], S. X. Hu[2], Jinsong Huang[3], and Yongli Gao[1*]

[1]Department of Physics and Astronomy, University of Rochester, Rochester, NY 14627

[2]Laboratory for Laser Energetics (LLE), University of Rochester, Rochester, NY 14623

[3]Department of Applied Physical Sciences, University of North Carolina at Chapel Hill, Chapel Hill, NC, 27599

* ygao@pas.rochester.edu

Supplementary Materials

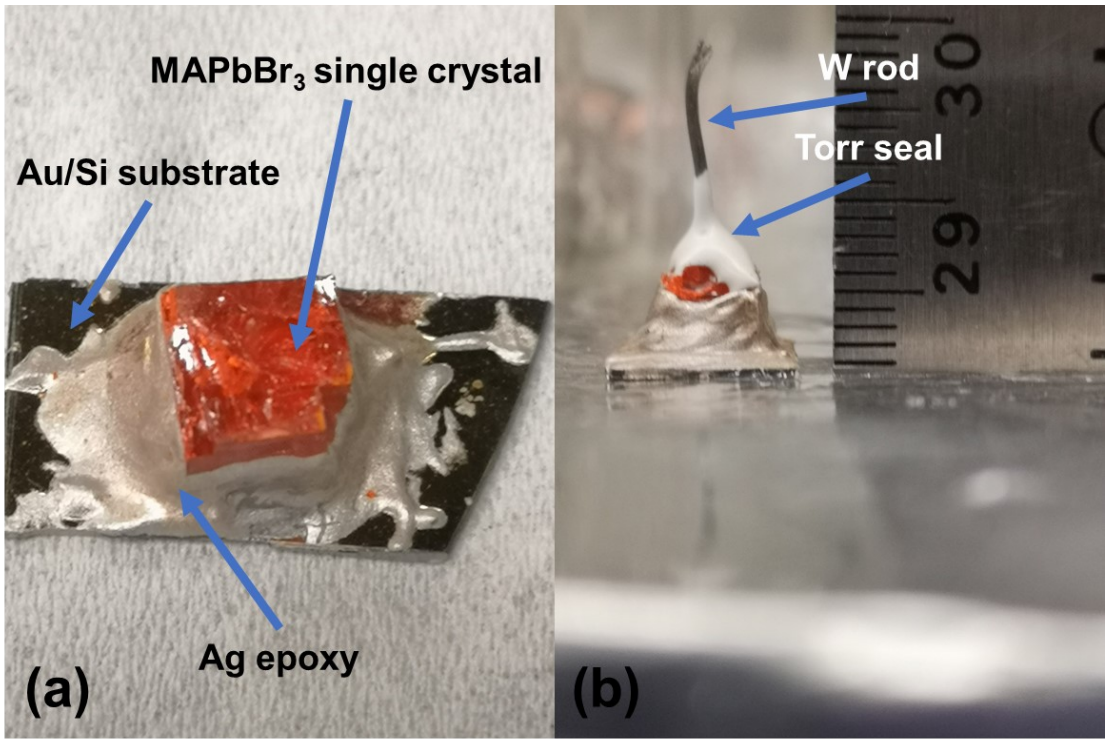

Figure S1. $MAPbBr_3$ single crystal cleavage preparation. (a) The crystal was glued on top of Au-coated silicon wafer by silver epoxy. (b) A tungsten rod was glued perpendicularly on top of perovskite surface by Torr seal.

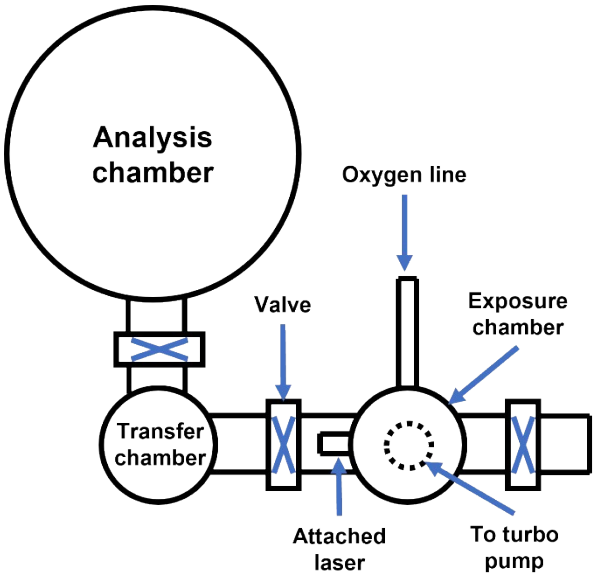

Figure S2. Top-view schematic of the UHV system.

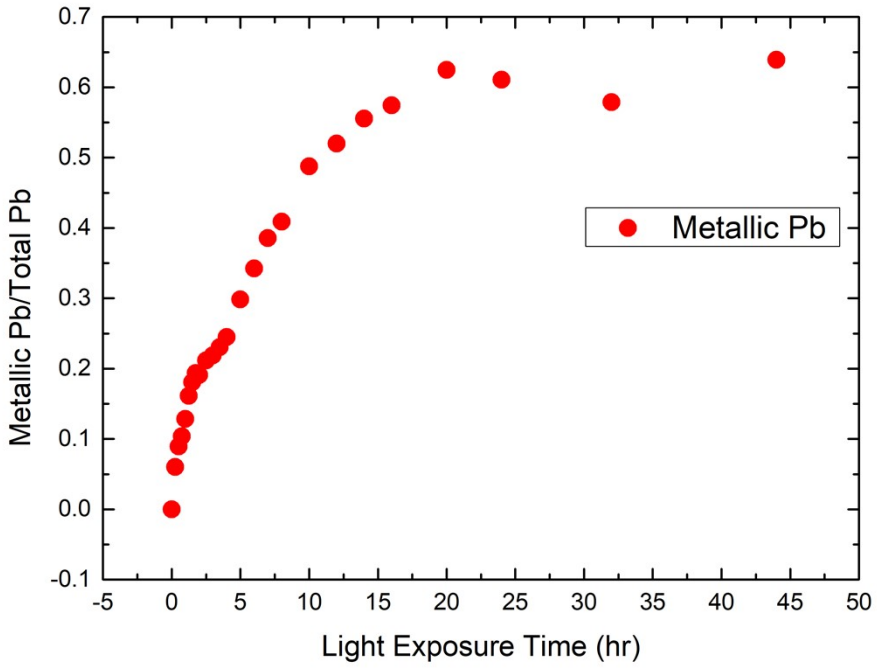

Figure S3. Metallic Pb ratio trend of light-only exposure.

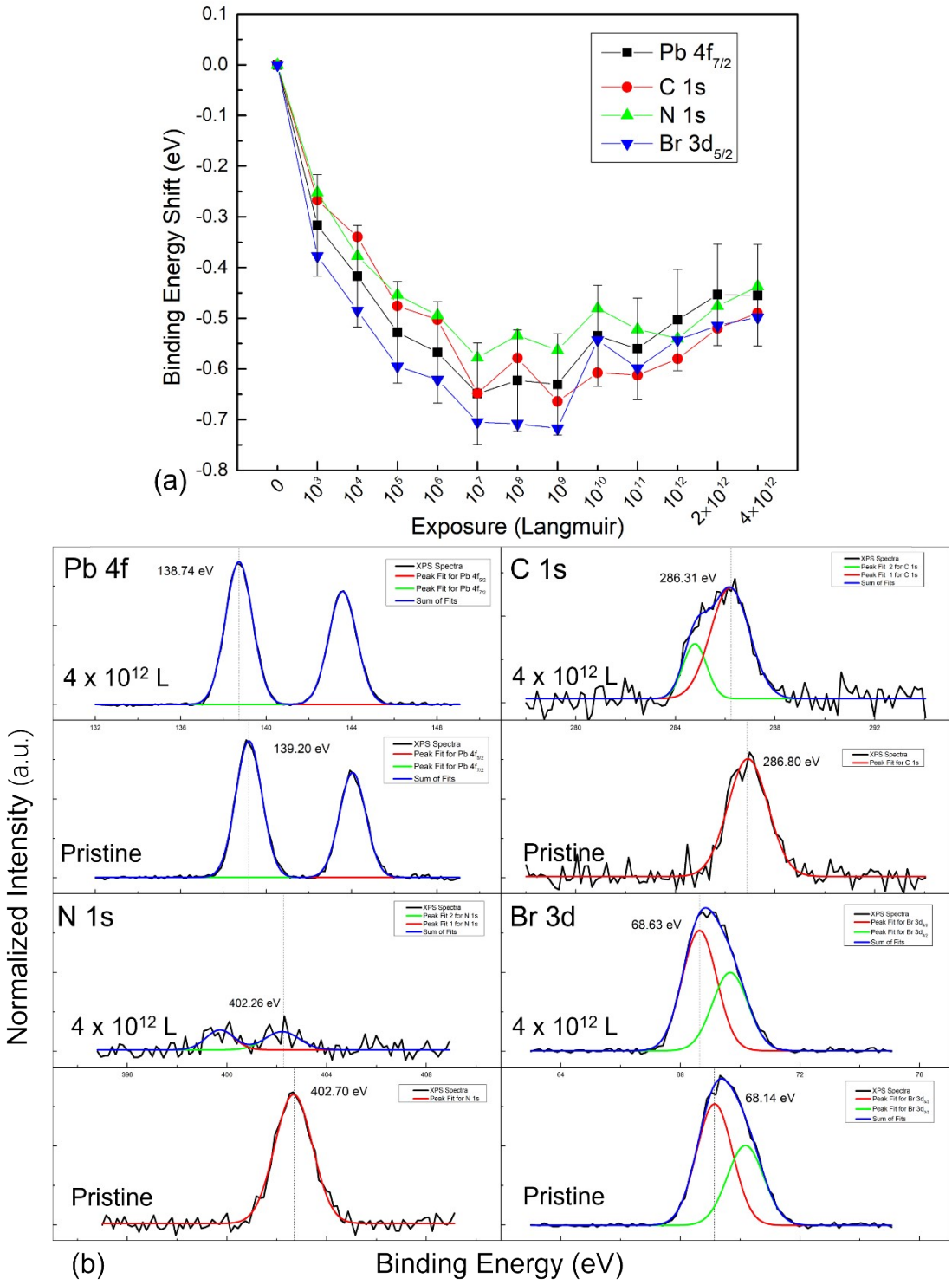

Figure S4. (a) Binding energy shift with exposures for Pb 4f, C 1s, N 1s and Br 3d core levels. (b) XPS spectra peak fitting for pristine and after-exposure core levels.

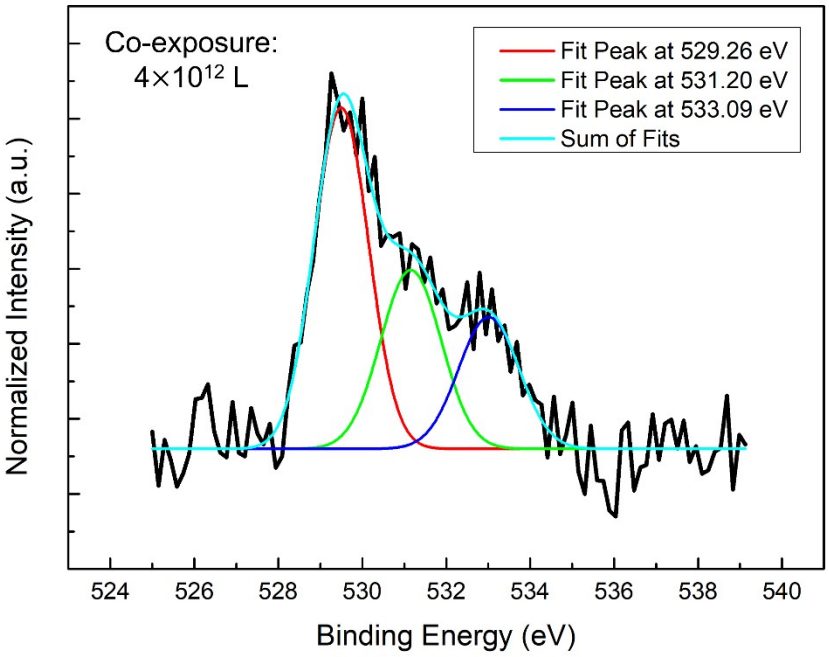

Figure S5. XPS spectra peak fitting for O 1s at 4×10^{12} L of co-exposure.

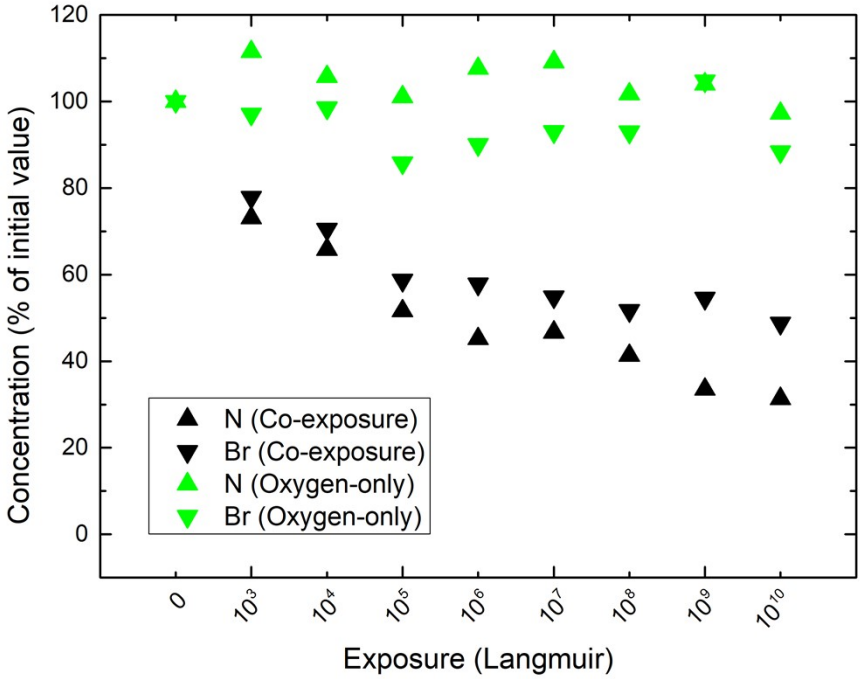

Figure S6. Comparison of N and Br ratio trend of co-exposure and oxygen-only exposure. It shows O_2 doesn't react with sample, as N and Br ratio remain stable.

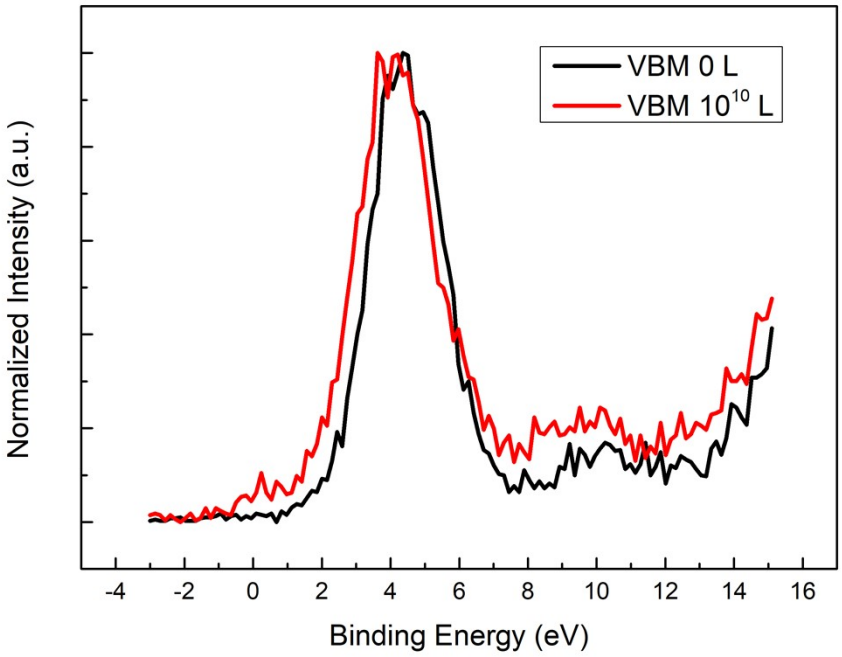

Figure S7. Comparison of VBM spectra of co-exposure at 0 L and 10^{10} L.

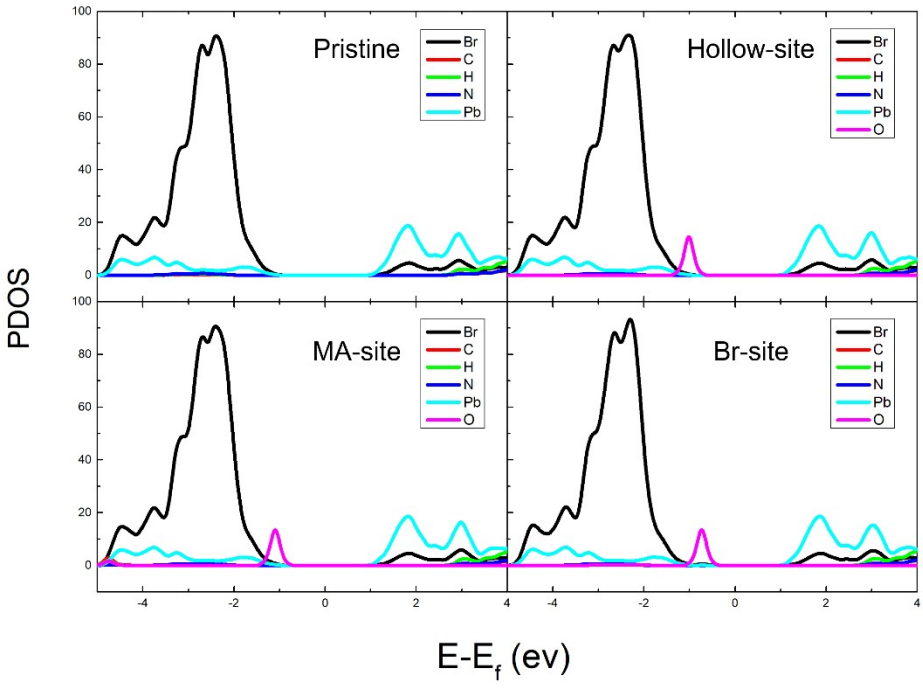

Figure S8. Projected densities of states (PDOS) of pristine MAPbBr3, hollow-site, MA-site and Br-site oxygen absorption models.

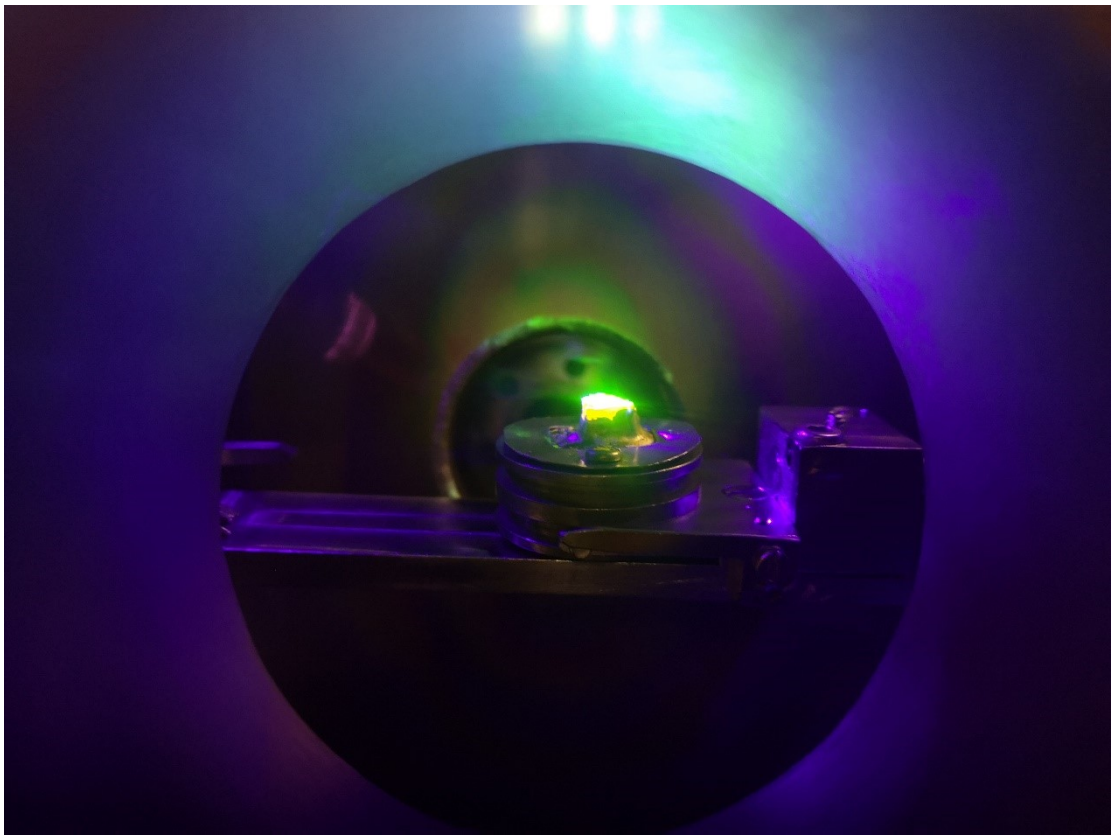

Figure S9. PL emission of the sample under light and oxygen co-exposure.

Table S1. Spectral normalization factors for Pb 4f, Br 3d, C 1s and N 1s core levels.

Exposure (L)/Norm. Factor (10^{-4})	Pb 4f	Br 3d	C 1s	N 1s
0	2.92	5.85	2.27	2.99
10^3	3.17	7.25	1.96	3.29
10^4	2.95	6.67	1.89	2.96
10^5	3.00	7.09	1.84	3.05
10^6	2.97	7.22	1.78	3.09
10^7	2.92	7.13	1.78	2.98
10^8	2.94	7.52	1.79	2.98
10^9	2.60	8.75	1.74	2.27
10^{10}	2.82	8.69	1.94	2.80
10^{11}	2.55	8.76	1.67	1.93
10^{12}	2.30	8.73	1.77	2.11
2×10^{12}	2.15	8.38	1.71	2.08
4×10^{12}	1.94	7.87	1.67	2.04

Sample Cleavage:

The crystal was first glued on the Au coated Si substrate with a conductive Ag epoxy. (Epoxy Technology, Product EJ2189-LV) When the epoxy was cured, another vacuum compatible epoxy (Varian Vacuum Technologies, Product Torr Seal) was applied to cover the top surface of the crystal, then a tungsten rod was perpendicularly mounted in the Torr seal. When the whole crystal sample was fully cured, it was loaded into the exposure chamber. Another transfer arm was used to break off the tungsten rod with the top layer of the crystal, so that the crystal was cleaved in-situ and a pristine surface was obtained.

Attenuation Length Estimation:

From the well-known universal curve of the photoelectron mean free path, we estimate that Pb 4f, C 1s, N 1s, Br 3d, and O 1s have attenuation lengths of 19.8, 18.7, 17.7, 20.3 and 16.7 Å, respectively, using the following equation[1]:

$$\lambda = \frac{143}{E^2} + 0.054 \times \sqrt{E}$$

Where λ is inelastic mean free path, E is kinetic energy of the photoelectrons.

Reference

1. M. P. Seah, W. J. S. Dench and i. analysis, 1979, **1**, 2-11.